ANALYTICAL SEPARATION AND QUANTITATION OF SPECIFICATION LEVELS OF MDA IN AVIATION FUELS

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INTRODUCTION

Metal deactivator additive (MDA) has been used for the past fifty years to chelate metals which accelerate oxidation reactions in distillate materials (1). Presently, MDA is added to aviation fuel in the concentration range of 0 - 5.8 mg/L. Because of its surface activity and adsorptive properties, MDA may be reduced in concentration as the fuel is handled. Also, as fuels are used to cool hotter aircraft engine components, metal concentrations may increase due to degradation of fuel system materials. Consequently, reduced concentrations of MDA may be insufficient to prevent accelerated autoxidation reactions. The ability to measure the concentration of MDA in storage stability tests, thermal stressing studies and additive addition in the field is important to the success of new thermal stability additives such as JP-8+100 (2).

This work describes a new technique for the determination of metal deactivator additive in aviation fuels and provides some examples of how this measurement can be used to understand the role and fate of MDA in thermally-stressed fuel systems. Several techniques are available in the literature which were not satisfactory for use with distillate fuels having high polars content , low levels of MDA, or for thermally stressed fuels (3,4,5). The technique described herein may be used for specification level analysis of small amounts of sample (200 µL) without analyte concentration or significant sample preparation.

Direct Analysis of MDA

Previous work has been performed in which gas chromatography - mass spectrometry (GC-MS) and similar chromatographic techniques were used to measure MDA concentration directly. However, the polarity and surface activity of MDA made direct detection impossible without specially deactivated chromatographic columns, split liners, and glass wool. Unfortunately, detection limits, detector linearity, and repeatability continued to be poor, even after the activities of these surfaces were reduced. Calibration curves for MDA in toluene indicated detection limits of 10 - 20 mg/L typically, with even higher detection limits for more complex solvent matrices. In order to lower the detection limits, silica gel solid-phase extraction (50:1 concentration) was performed for most aviation fuel samples, concentrating the polar fuel components and improving detectability. Although this technique was used to track MDA disappearance in thermally stressed systems, sample preparation time and reproducibility/repeatability were unacceptable.

Chemical Derivatization

The analysis of MDA was performed by reacting this highly adsorptive polar compound with the silylating agent N,O-bis[trimethylsilyl]acetamide (BSA) to form the derivatized product as shown:
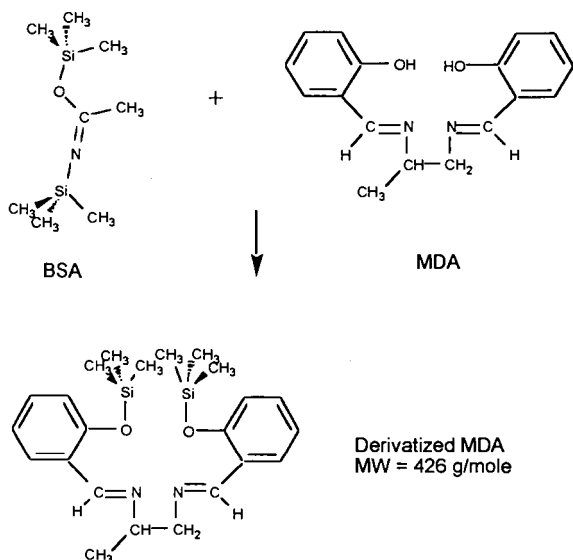
Figure 1. Derivatization reaction of N,O-bis [trimethylsilyl] acetamide (BSA) with MDA.

BSA is a common trimethylsilyl donor which reacts to replace active hydrogens from phenols, acids, thiols and amines with the trimethylsilyl functionality (7). These reactions typically occur in nearly 100% yields; in this case, no MDA or partially silylated compounds were detectable after reaction. The reaction occurs at room temperature and although the resultant derivatized compound has a molecular weight of 426 g/mole, its non-polar nature allows it to be eluted from typical non-polar chromatographic columns at temperatures similar to MDA elution.

EXPERIMENTAL

MDA from a 75% mixture in aromatic solvents (Octel America) was used to make standard mixtures in a reference kerosene (Aldrich Chemical) at concentrations between 0 and 10 mg/L. Two hundred microliters of each solution were pipetted into glass micro-inserts and sealed in a GC vial (Hewlett Packard). A 10 µL full scale syringe (Hamilton) was used to add 5 µL of BSA (Pierce) to each sample. Care was taken to minimize exposure of the BSA to atmospheric moisture since BSA is highly reactive with water. Finally, each solution was mixed for approximately 10 seconds on a vortex mixer.

The GC-MS (Hewlett Packard 5890/5971) was operated in the selected ion monitoring mode (220, 235 amu) for the majority of the analyses. The gas chromatograph was programmed linearly from 150 (1 minute hold) to 280°C (5 minute hold) at 10°C per minute. The chromatographic column was a 30 meter, 0.25 mm ID, 0.25 micron film thickness HP-5 capillary column (Hewlett Packard), although almost any non-polar column having a thermal stability greater than 300°C would be suitable. Preliminary analyses indicated that a thin film (0.1 micron film thickness) column may be desirable for both resolution and analysis time. Interferences (from fuel or stressed fuel components) were separated from the derivatized MDA signal by knowledge of the correct retention time as well as the specificity of the selected ions and the ion ratios. The 220 and 235 ions were used for MS quantitation; these ions were the strongest ions in the mass spectrum for the MDA derivative.

RESULTS AND DISCUSSION

Calibration work indicated that this technique could be used to measure specification levels of MDA in hydrocarbon matrices. Figure 2 shows typical calibration curves between 0 and 10 mg/L MDA, demonstrating the linearity of the detector and the quantitative yields from the addition of BSA to each calibration solution. One should note that the intercept for the curve is

non-zero, indicating a lower detection limit of approximately 0.5 mg/L, possibly due to adsorption of the MDA on the glass vial before the BSA is added.
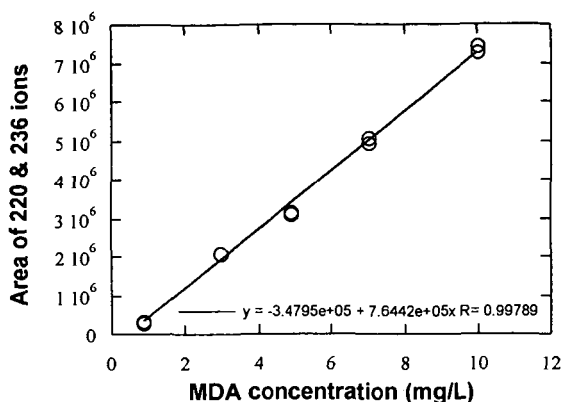

Figure 2. Typical calibration for derivatized MDA in a reference kerosene.

The lower detection limit (approximately 0.5 mg/L) of MDA as shown in figure 2 was affected by the adsorption of MDA to the glass insert and other surfaces to which the MDA is exposed. If BSA is added to a 10 mg/L MDA solution and the derivatized MDA serially diluted with kerosene to produce analytes between 0 and 1 mg/L, the minimum detectable level of MDA derivative is greatly decreased and linearity of detection greatly improved. This observation is consistent with MDA being adsorbed to active sites in the glass vial which have high surface to volume ratios, affecting the lower level standards more than higher level standards. The use of plastic inserts did not improve the amount of MDA adsorbed before it could be derivatized. Further studies may be conducted to see if surface deactivation (using an MDA wash solution) would enhance lower level detection of the additive.

Effect of Fuel Matrix on Measurement

A series of Jet A and JP-5 aviation fuels were spiked with a known amount of MDA. These samples were treated with BSA and duplicate measurements of each were used to quantitate the level of MDA (see Table 1). No history of the origin of the fuel was available; levels of MDA which may have already existed in the fuel were not available and could not be traced.

Table 1
Results of Analysis of Samples Spiked with MDA

Sample ID	Fuel type	MDA added (mg/L)	MDA measured (mg/L)
POSF-2985	Jet A	2.0	2.0
POSF-2963	JP-5	2.0	2.2
POSF-2963	JP-5	6.0	5.0
POSF-3119	Jet A	2.0	2.7
POSF-3084	Jet A	2.0	2.8
POSF-2926	Jet A	2.0	2.4
POSF-2827	Jet A	2.0	2.8
POSF-3059	Jet A	2.0	2.5
POSF-2962	JP-5	6.0	6.0
POSF-2962	JP-5	2.0	2.5

All of the measurements obtained (POSF-2963 as an exception) were greater than or equal to the amount added to the original fuel. We suspect that these fuels may have been doped with MDA at the refinery (up to 5.8 mg/L is allowable). As the history of each fuel was unknown, all samples were reanalyzed with BSA alone to detect low levels of MDA. With the exception of POSF-2962, all samples showed small amounts of uncomplexed MDA present (less than 0.5 mg/L). Attempts were made to quantify the MDA, but the calibration curve was non-linear

between 0 and 1 mg/L due to adsorption of the small amounts of MDA on surfaces. Further work needs to be conducted to improve the low level accuracy (and precision) of this technique.

Samples POSF-2962 and POSF-2963 were of considerable interest because it is not known whether MDA that is chelated with a metal in solution can also be silylated. To examine this question, POSF-2962 was spiked with copper naphthenate (to 100 ppb copper) and renamed POSF-2963. This fuel (POSF-2963) was measured by ICP-AES to have a copper content of 98 parts-per-billion (ppb), with iron and zinc levels measured at 60 and 14 ppb, respectively. Because the mass spectrometer was used to detect a specific mass at a specific retention time, MDA complexed with copper and silylated should not be detected at the same retention time as MDA not complexed with copper. Therefore, POSF-2962 should have higher levels of MDA measured than its counterpart, POSF-2963, which was subjected to copper. This was indeed the case as shown in Table 1 for fuel spiked at the 2.0 and 6.0 mg/L levels of MDA: in each case, MDA concentration was higher in the POSF-2962 sample than the POSF-2963 sample. Further studies (using fuels with known processing histories) will be conducted to determine the chemistry of derivatization reactions for copper-containing MDA.

Measurement of Field Samples for Additive Content

An additive package currently being investigated for Air Force fuels, JP-8+100, is comprised of several additives including a detergent/dispersant, antioxidant and the metal deactivator additive, MDA. Because the additive is introduced in the field at the user level, measurements of the level of MDA could provide an important check on the techniques used to deliver and mix the additive package. Four samples were obtained from active air bases currently using the JP8+100 additive and were received in undeactivated one gallon cans. Results from the four samples indicated that MDA concentrations were below the desired level of 2.0 mg/L with most measurements indicating less than 1 mg/L. Because field sampling cans have a low surface to volume ratio, one would probably suspect the glass containers used in the laboratory for the poor recovery of MDA. Additional work will address the possible deactivation of these surfaces so that field sampling of the additive package will predict or indicate problems in the field.

Tracking Additive Concentration During Stressing Tests

Thermal stressing may decrease additive concentration in some fuels, so the ability to track additive concentration is of interest. Figure 3 shows that the MDA concentration decreases as a function of time with oxidative stressing at 180°C. MDA concentration decreases as a function of time due to its reaction with other species. As MDA reacts it may become less effective as a chelation additive, and therefore unable to complex metals which may increase in concentration during stressing due to materials degradation (7).
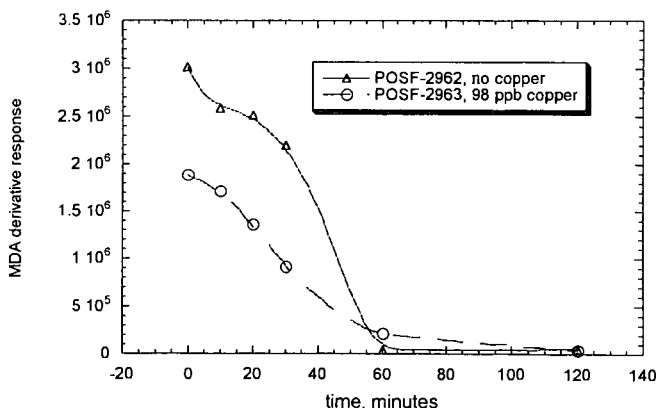
Figure 3. MDA reaction during thermal stressing of neat and copper-doped fuel in the Isothermal Corrosion Oxidation Tester.

CONCLUSIONS

Metal deactivator additive (and potentially, other phenolic additives) can be successfully analyzed using chemical derivatization followed by GC-MS detection. Because of the surface active nature of MDA, conventional chromatographic techniques are prone to poor accuracy and precision, as well as high detection limits. Derivatization with BSA can be conducted at room temperature using extremely small samples (200 µL) with sensitivity sufficient to cover the specification range of the additive. Analysis time due to selected ion monitoring on the GC-MS can be as short as 13 minutes. Consequently, this technique can be used to evaluate additive concentrations in the field, track additive usage in stressing studies and to understand the relationship between metal deactivator additive and surfaces or metals in the fuel.

ACKNOWLEDGMENTS

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